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OCT 79 K C MOLLOY , J J ZUCKERMAN N00014-77-C-0432
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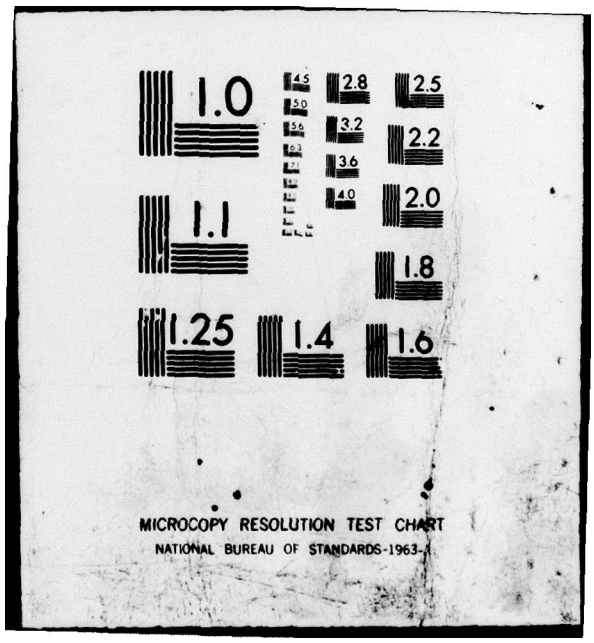
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SECURITY CLASSIFICATION OF THIS PAGE (When Data Entered)

REPORT DOCUMENTATION PAGE

READ INSTRUCTIONS BEFORE COMPLETING FORM

1. REPORT NUMBER: 13

2. GOVT ACCESSION NO.

3. RECIPIENT'S CATALOG NUMBER

4. TITLE (and Subtitle): (6) Variable Temperature ^{119m}Sn Mössbauer Study of Organotin - Substituted Styrene Monomers and Polymers.

5. TYPE OF REPORT & PERIOD COVERED

6. PERFORMING ORG. REPORT NUMBER

7. AUTHOR(s): (10) K. C. Molloy, J. J. Zuckerman, H. Schumann, G. Rodewald

8. CONTRACT OR GRANT NUMBER(s): (15) N00014-77-C-0432

9. PERFORMING ORGANIZATION NAME AND ADDRESS
University of Oklahoma
Department of Chemistry
Norman, Oklahoma 73019
403 180

10. PROGRAM ELEMENT, PROJECT, TASK AREA & WORK UNIT NUMBERS
NR 053-636

11. CONTROLLING OFFICE NAME AND ADDRESS
Office of Naval Research
Department of the Navy
Arlington, Virginia 22217

12. REPORT DATE: (11) 1 Oct [redacted] 79

13. NUMBER OF PAGES: 6

14. MONITORING AGENCY NAME & ADDRESS (if different from Controlling Office): (12) 8 (14) TR-13

15. SECURITY CLASS. (of this report): Unclassified

15a. DECLASSIFICATION/DOWNGRADING SCHEDULE

16. DISTRIBUTION STATEMENT (of this Report)

Approved for Public Release, Distribution Unlimited

17. DISTRIBUTION STATEMENT (of the abstract entered in Block 20, if different from Report)

Prepared for Publication in Inorganic Chemistry

DDC RECEIVED OCT 31 1979 D

18. SUPPLEMENTARY NOTES

(9) Technical repts.

19. KEY WORDS (Continue on reverse side if necessary and identify by block number)

Organotin-Substituted Styrenes, Styrene Polymers, Mössbauer Spectroscopy, Tin-119m Mössbauer Spectroscopy, Variable Temperature Mössbauer Spectroscopy, Lattice Dynamics, Polymerization.

(119M)

20. ABSTRACT (Continue on reverse side if necessary and identify by block number)

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79 10 31 030

DD FORM 1 JAN 73 1473 EDITION OF 1 NOV 65 IS OBSOLETE
S/N 0102-LF-014-6601

403 180

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SECURITY CLASSIFICATION OF THIS PAGE (When Data Entered)

OFFICE OF NAVAL RESEARCH

Contract N00014-77-C-0432

Task No. NR 053-636

TECHNICAL REPORT NO. 13

Variable Temperature ^{119m}Sn Mössbauer Study of Organotin - Substituted Styrene Monomers and Polymers.

by

K. C. Molloy and J. J. Zuckerman
H. Schumann and G. Rodewald

Prepared for Publication

in

Inorganic Chemistry

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Variable Temperature ^{119m}Sn Mössbauer Study of Organotin - Substituted Styrene Monomers and Polymers.

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SUMMARY

Variable temperature ^{119m}Sn Mössbauer spectroscopy can detect the enhanced binding of the tin atom in organotin(IV)-substituted styrenes on polymerization.

Tin-containing organometallic polymers (OMPs) are being actively investigated as potential marine antifouling materials. The OMPs are unique in containing the organotin pesticide chemically bound to a polymer backbone, resulting in controlled release into the marine environment.[1] The binding at the tin site is crucial to the rate at which the resease will take place. We report here the first application of a method based upon Mössbauer spectroscopy for distinguishing the state of binding of the tin atoms in organotin-substituted monomers and polymers.

Di-*para*-totyldi-*para*-styryltin(IV) (I) (mp 83-84°C) and tetra-*para*-styryltin(IV) (II) (mp 134.5-135.5°C) are solids formed by treatment of the corresponding tin chloride with the *para*-styryl Grignard reagent. The monomers are polymerized to (Ia) and (IIa) by gentle heating to infusible solids.[2] The tin-119m Mössbauer Isomer Shift (IS) and Quadruple Splitting (QS) values for the monomers (I: IS=1.23±0.02; QS=0mm/s and II: IS=1.17±0.02; QS=0mm/s) do not change outside of experimental error on polymerization (Ia: IS=1.21±0.02; QS=0mm/s and IIa: IS=1.20±0.02; QS=0mm/s).[3] These values are typical of simple tetraorganotin compounds,[4] and the failure to detect any change in their magnitudes on polymerization has been noted before for trimethyl-[5] and triphenyl-*para*-styryltin(IV).[6]

It has been recently found that logarithmic plots of the Mössbauer resonance areas *vs.* temperature are linear over an accessible temperature range as expected according to the Debye model of solids in the high temperature limit. For a thin absorber the recoil-free fraction, f(T), is directly related to this area, A(T), and may be used to investigate the lattice dynamics at the tin site. It is found that the more tightly bound the tin atoms, the slower will be the decrease in f, and hence A(T), as the temperature is raised. Compounds of known structure, consisting of non-interacting monomeric molecules exhibit slopes $[a = \frac{d\ln (A_T/A_{77})}{dT}]$ of *ca.* $-1.8\times10^{-2}K^{-1}$. Solids in which one-, two- or three- dimensional association is present exhibit slopes of *ca.* $-0.9\times10^{-2}K^{-1}$ or less.[7]

Figure 1 displays the logarithmic plot of the area under the Mössbauer resonances, normalized to 77K for ease of comparison of data, *vs.* temperature

in the range 77 to 140K for monomers I and II and their polymers Ia and IIa. The spectral intensities in the case of the monomers decays rapidly [I:a=-2.13x10^{-2} K^{-1} (regression analysis, r=-0.990, intercept 1.64, 4 points); II: a=-2.08x10^{-2}K^{-1} (-0.998, 1.60, 3)], and it becomes impossible, even over extremely long counting times, to obtain usable data above ca. 100K. By contrast the spectral intensities for the materials after polymerization show slower decays [Ia: a=-1.79x10^{-2}K^{-1} (r=-0.993, 1.36, 8); IIa: a=-1.95x10^{-2}K^{-1} (r=-0.999, 1.51, 6)], and spectra can be obtained up to ca. 140K.

The effect of polymerization in locking the tin atom in its position must necessarily be very small, yet the effect is detectable by Mössbauer techniques in two ways. Firstly, the temperature dependences of the recoil-free fractions are discernably greater for the monomers than for their polymers. Secondly, the Debye model by which the slopes in Figure 1 are linear, itself begins to break down, and for the monomers the resonance areas above ca. 100K are very much smaller than expected by extrapolation of the linear plots in the range 77 to 100K.

While the tin atoms are clearly more free to move in the monomers, the added constraint on polymerization is not as marked as when tin atoms are bound rigidly by bridging, directly-attached electronegative substituents.[7] In the case of the tetraorganotins studied here, the tin atoms continue to be held by bonds to four carbons and, moreover, the polymerized lattice itself may itself be quite porous owing to the steric bulk of the atoms attached to tin.

Acknowledgement.

Our work is supported by the Deutsche Forschungsgemeinschaff, Bonn-Bad Godesberg and the Fonds der Chemischen Industrie, Frankfurt (to H.S.) and by the Office of Naval Research (to J.J.Z.). We thank especially the Scientific Affairs Division of NATO for a grant which makes this collaboration possible.

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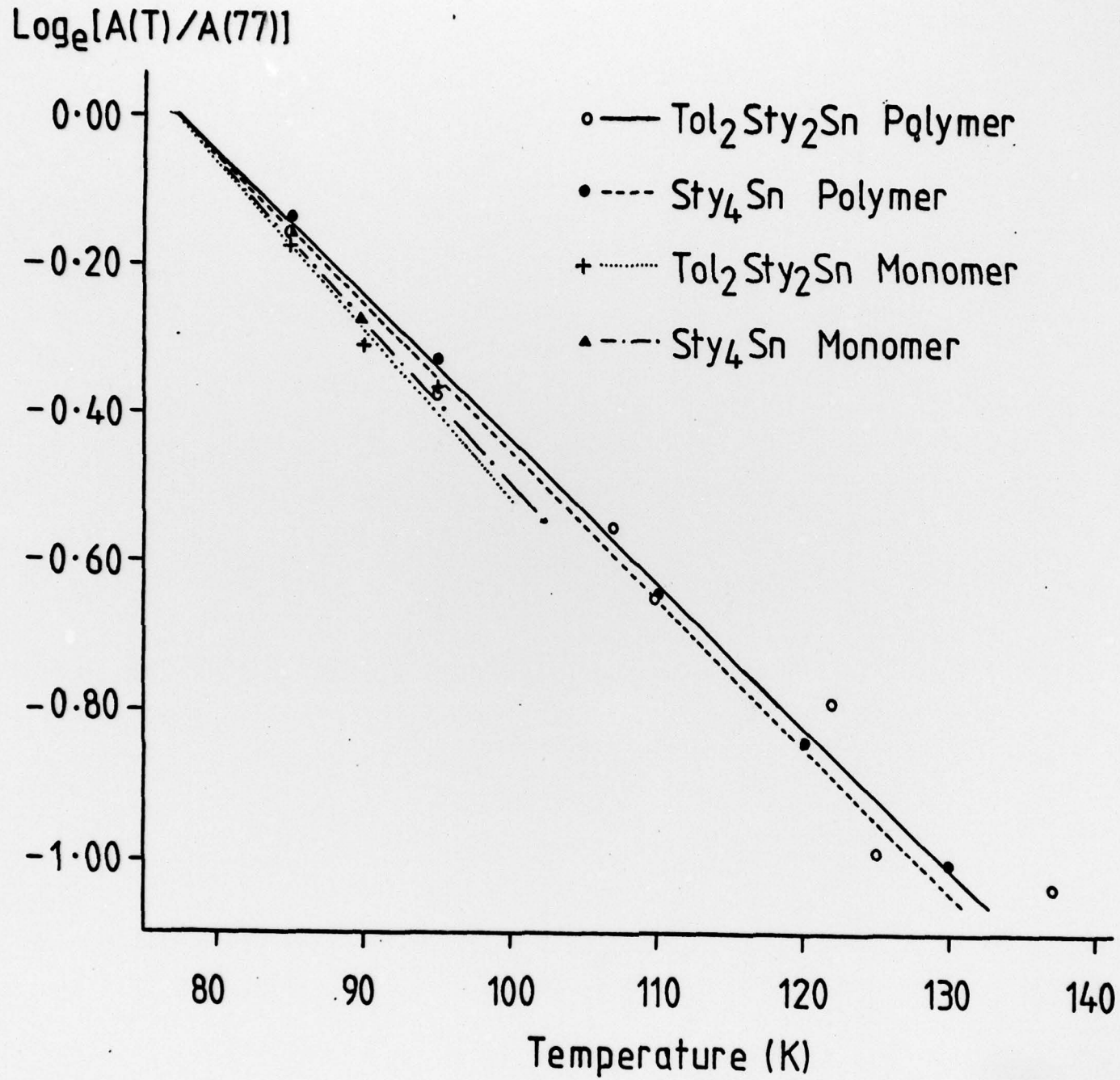
Figure Caption

Figure 1. Logarithmic plot of the area under the Mössbauer resonances [A(T)] normalized to 77K *vs.* temperatuer in the range 77 to 140K for Di-*para*-tolyldi-*para*-styryltin(IV) and tetra-*para*-styryltin(IV) and their polymers.


Log$_e$[A(T)/A(77)]
0·00
-0·20
-0·40
-0·60
-0·80
-1·00
80
90
100
110
120
130
140
Temperature (K)
Tol$_2$Sty$_2$Sn Polymer
Sty$_4$Sn Polymer
Tol$_2$Sty$_2$Sn Monomer
Sty$_4$Sn Monomer